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(54) Filled polyolefin compositions

(57) A composition comprises 0-80% by weight of a homopolymer of ethylene and/or copolymer of ethylene with at least one C_3-C_{10} alpha-olefin, 10-70% by weight of a modified polyethylene and 10-70% by weight of aluminum silicate that has been surface treated with an amino-silane compound. The modified polyethylene is formed by grafting at least one of an ethylenically unsaturated carboxylic acid or anhydride on to polyethylene. The compositions exhibit stiffness and toughness properties that are superior to those obtained with unfilled polyethylene, and may be used in injection moulding, sheet forming, blow moulding and related processes to produce, for example, containers, sports and recreation equipment, transportation and packaging equipment and the like.

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TITLE

ALUMINUM SILICATE-FILLED POLYOLEFIN COMPOSITIONS

The present invention relates to filled thermoplastic polymer compositions and especially to filled polyolefin compositions adapted to be fabricated into articles having stiffness and toughness properties that are superior to those obtained with articles of the un-filled polyolefin; as used herein, toughness refers in particular to impact strength and ultimate tensile strength properties. The filler is a modified aluminum silicate. As used herein, aluminum silicate includes both synthetic aluminum silicates and naturally occurring aluminum silicates e.g. clay and kaolin.

Polyolefins are used in a wide variety of end uses, including in the form of film, fibres, moulded or thermoformed articles, pipe and/or coatings. In some end-uses, especially when the polyolefin is fabricated into articles by moulding, extrusion or thermoforming techniques, it is important that the fabricated article exhibit stiffness and toughness properties that are superior to those obtainable from the polyolefin per se. Techniques for modification of the properties of polyolefins are known, including cross-linking the polymer or incorporating additives or fillers into the polymer. Articles formed from filled thermoplastic polymer compositions tend to exhibit a higher stiffness than articles manufactured from the corresponding un-filled polymer, but such an increase in stiffness with filled compositions is usually accompanied by a decrease in other important properties, including toughness.

Filled thermopolastic polymer compositions containing a so-called "reinforcement promoter" are known, and are discussed in published European patent

application No. 257 796 of M.G. Dokurno, D.A. Harbourne, and E. M. Lundhild, published 1988 March 02. In addition, that publication discloses a composition comprising 30-90 parts by weight of a polyolefin, 10-70 parts by weight of a modified polyethylene and 20-70% by weight based on the amount of polymer of at least one filler selected from magnesium hydroxide, calcium hydroxide, alumina trihydrate, hydroxyl-containing carbonates of magnesium and hydroxyl-containing carbonates of calcium. The modified polyethylene is formed by grafting at least one ethylenically unsaturated carboxylic acid or anhydride thereof onto a polyethylene. Other filled compositions are discussed in that patent publication.

U.S. Patent 4 711 673 of L.L. Musselman et al, issued 1987 December 08, discloses a filler composition containing at least two surface modifiers and comprising a powdered inorganic filler, a carboxylic acid or mixture of carboxylic acids and an organosilane. Preferred organosilanes are stated to be vinyl-tris(2-methoxyethoxy) silane, organosilane esters and methyl vinyl siloxane fluid. The filler composition may be blended with thermoplastic polymers.

Japanese 57 172 940 of F. Iwami et al, published 1982 October 25, discloses compositions that are obtained by admixing an inorganic filler that has been pre-coated with an organosilane compound, a polyolefin (polypropylene), an unsaturated carboxylic acid and an organic peroxide, in the presence of a dispersing agent and an antioxidant. The resultant compositions are stated to have excellent mechanical strength and heat resistance, the examples illustrating compositions having Izod impact strengths of 6.5 kg.cm/cm (63.8 Joules/m).

It has now been found that compositions of

improved impact strength may be obtained using compositions of polyolefin, modified polyethylene and amino silane-treated aluminum silicate.

Accordingly, the present invention provides a composition comprising:

(a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin, and mixtures thereof;

(b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and

(c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound.

In a preferred embodiment of the composition of the present invention, the ethylenically unsaturated carboxylic acid is maleic acid and the ethylenically unsaturated carboxylic acid anhydride is maleic anhydride.

The present invention also provides a process for the manufacture of a polyolefin composition, comprising:

(i) feeding to apparatus adapted for the admixing of molten thermoplastic polymers with other materials, an admixture of: (a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of

homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin, and mixtures thereof; (b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and (c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound;

(ii) admixing (a), (b), and (c) at a temperature above the melting point of the polymers of (a) and (b), said temperature being below the temperature of decomposition of both said filler and the polymers of (a) and (b); and

(iii) extruding from the apparatus a composition formed from (a), (b) and (c).

The present invention also provides a process for the manufacture of articles comprising the steps of feeding a composition to extrusion or moulding apparatus, and forming said article by extruding or moulding said composition into a shaped article and cooling the article so formed, said composition comprising:

(a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin, and mixtures thereof;

(b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from the group consisting of homopolymers of ethylene and co-polymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and
(c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound.

~~The present invention also provides articles~~ manufactured using the processes described herein.

In embodiments of the compositions, processes and articles of the present invention, a portion of the aluminum silicate is replaced with a second filler.

In another embodiment of the compositions, processes and articles of the present invention, a portion of the polymeric component is replaced with a polar polymer.

The polyolefin of the composition of the present invention is comprised of 0-80% by weight of homopolymers of ethylene and/or copolymers of ethylene with at least one C_3-C_{10} hydrocarbon alpha-olefin. Examples of such alpha-olefins are propylene, butene-1, hexene-1 and octene-1. The density of the polyolefin will normally be in the range of about 0.895 to 0.965 g/cm^3, especially in the range of 0.920-0.960 g/cm^3. The melt index of the polyolefin is preferably in the range of 0.5-20 dg/min, especially in the range of 0.5-15 dg/min.

The density and melt index of the polyolefin

used to form the compositions of the invention may be varied over a wide range and will depend, in particular, on the intended end-use of the articles formed e.g. by injection moulding techniques, from the compositions. Higher densities will tend to give relatively stiff articles whereas lower densities will tend to give more flexible articles.

The compositions of the invention also contain a modified polyethylene. The polyethylene of the modified polyethylene is a homopolymer of ethylene and/or a copolymer of ethylene and at least one C_4-C_{10} hydrocarbon alpha-olefin. Examples of such alpha-olefins are butene-1, hexene-1, and octene-1. The polyethylene is modified by grafting the polyethylene with at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride. Preferably the acid is maleic acid and the anhydride is maleic anhydride. The polyethylene that is modified by grafting should have a density of at least 0.910, preferably 0.920 g/cm^3 and in particular at least 0.950 g/cm^3, especially as the filled compositions formed using such modified polyethylene tend to exhibit flexural modulus properties that are superior to the unfilled polymer.

Techniques for the preparation of grafted copolymers are known in the art, preferred examples of which are disclosed in published European Patent Application No. 0 172 650 of G. White, published 1986 February 26, and in U.S. Patent 4 612 155 of C.S. Wong and R.A. Zelonka, which issued 1986 September 16. Grafted copolymers may also be prepared by the thermal reaction of maleic anhydride with polyethylene or elastomers at temperatures of at least about 375°C.

The modified polyethylene should have between 0.05 and 5.0%, by weight, of monomer grafted onto the backbone thereof, and especially between 0.2 and 2.0%

of grafted monomer. Both the amount of grafted monomer on the polyethylene and the amount of the grafted polyethylene in the composition will affect the flow properties of the compositions of the invention. For instance, higher amounts of grafted monomer will result in higher interactions between the grafted monomer and the filler, and consequently a decrease in the flowability of the compositions. This may be advantageous for some processes e.g. extrusion and blow moulding processes, and disadvantageous for other processes e.g. injection moulding processes. Amounts of grafted monomer below 0.2 and especially below 0.05% by weight may not provide sufficient improvements in the toughness of the resultant products.

The compositions of the invention contain 0-80% by weight of the composition of polyolefin and 10-70% by weight of the composition of modified polyethylene, and especially 30 to 60% by weight of polyolefin and 20 to 50% by weight of the modified polyethylene.

The compositions of the invention also contain 10-70% by weight of the composition of aluminum silicate filler that has been treated with an amino silane compound so as to modify the surface of the filler. Examples of such fillers are available as Translink* 445 and 555 from Engelhard Corporation of Edison, NJ, U.S.A. Translink fillers are described in literature from the manufacturer as surface modified calcined aluminium silicates, the surface modification providing hydrophobicity and dispersion properties. Translink 445 grade is stated to be designed to be compatible with polyamides, polyesters and other polar polymers, and to reduce water absorption, increase tensile and flexural strength, increase the heat deformation temperature and increase temperature

* denotes trade mark

stability. Translink 555 grade is stated to be similar but with a finer particle size to increase impact strength and flexural modulus.

In embodiments of the invention, the aluminum silicate filler is prepared by calcining air-classified or water-classified ground kaolin, in order to dehydrate the kaolin, and then treating the resultant product with the amino-silane compound. The amino silane may of the formula $R\text{-}Si\text{-}X_3$ where R is an organofunctional group, especially an alkyl radical, and X is a hydrolyzable group e.g chlorine, methoxy, ethoxy or acetoxy, and at least one of X and R contains an amino radical. An example of such a compound is 3-aminopropyl trimethoxy silane viz. $H_2NCH_2CH_2CH_2Si(OCH_3)_3$. The hydrolyzable radical is believed to react with -OH groups on the surface of the filler particle, and the amino radical is believed to provide a site that will react with the monomer grafted on the polyethylene.

In preferred embodiments, the compositions contain between 20 and 50% by weight of the aluminum silicate filler. The particle size of the filler may be important. It is known in the art that fine particle size fillers tend to provide products of higher impact strength than larger particle size fillers.

The compositions of the invention may be manufactured by feeding the components of the composition to apparatus adapted for the admixing of thermoplastic compositions. In particular, such components may be fed to a twin-screw extruder, a high-intensity fluxing mixer e.g. a Gelimat* mixer or a Farrell* continuous mixer. All of such apparatus is adapted for intensive mixing or compounding of compositions. The apparatus is operated at temperatures above the melting point of the polymers

* denotes trade mark

of (a) and (b) viz polyolefin and modified polyethylene, and above the melting point of polar polymers, if present.

After admixing the compositions, the compositions may be fed directly to apparatus for the manufacture of articles, especially injection moulding apparatus or apparatus for the extrusion of sheet or other profiles or blow moulding apparatus. However, the compositions will usually be first formed into comminuted shapes, for example, into pellets and other comminuted shapes, and subsequently fed to apparatus for the manufacture of articles.

The compositions may be subjected to a number of processes, especially injection moulding processes, sheet-forming and blow-moulding processes. In particular, the compositions may be injection moulded or formed into articles that have a useful combination of toughness and stiffness for many end-uses. For instance, the articles may be useful for sports and recreation equipment, safety and personal protection equipment, transportation and packaging equipment, blow moulded containers and the like.

The present invention is illustrated by the following examples:

Example I

A number of compositions were made from SCLAIR* 2907 polyethylene, which is an ethylene homopolymer having a density of 0.960 g/cm^3 and a melt index of 5.0 dg/min.

The compositions were made using a twin-screw compounding extruder from the polyethylene and one or more of the following:

(a) MA-g-2909, an experimental grafted polymer formed by melt grafting polyethylene with 0.62% by weight of maleic anhydride, the polyethylene being SCLAIR 2909 polyethylene, a homopolymer of ethylene having a

* denotes trade mark

density of 0.960 g/cm^3 and a melt index of 13.5 dg/min;

(b) Zytel* 101 polyamide, a nylon 66 (polyhexamethylene adipamide polymer) available from Du Pont Canada Inc.;

(c) Translink 555, an amino-silane surface treated aluminum silicate having an average particle size of 0.8 microns and a pH of 8.5-9.5;

(d) Translink 445, an amino-silane surface treated aluminum silicate having an average particle size of 1.4 microns and a pH of 8.5-9.5;

(e) Micropflex* 1200, a surface treated talc filler available from Pfizer Minerals Division;

(f) Huber 70C calcined kaolin, an unmodified clay with median particle size of 1.5 microns;

(g) Huber 80C calcined kaolin, an unmodified clay with median particle size of 1.2 microns.

Notched Izod impact strength was measured at 23'C and at -40'C using the procedure of ASTM D-256. The bars used were injection moulded at 200'C, except for compositions containing the polyamide which were moulded into bars at 290'C. The bars had a thickness of 0.32 cm. Flexural modulus was measured at 23'C using the procedure of ASTM D-790. Tensile strength and elongation were measured using the procedure of ASTM D-638, using Type IV dumbbells specified in that procedure.

Further details and the results obtained are given in Table 1.

* denotes trade mark

TABLE I

Run* No.	Grafted Polymer Amount (%)	Polyamide Amount (%)	Filler Type	Filler Amount (%)
1	-	-	-	-
2	43.3	-	-	-
3	-	-	c	30
4	-	-	f	30
5	-	-	g	25
6	30	-	c	30
7	26	-	c	40
8	30	-	d	30
9	26	-	d	40
10	30	10	c	30
11	25	20	c	30
12	30	10	d	30
13	30	-	c) e)	30) 10)

Note: The amounts shown are on the basis of the final composition

TABLE I (cont.)

Run No.	Notched Izod Impact Str. (Joules/m) 23'C	Notched Izod Impact Str. (Joules/m) -40'C	Flexural Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
1	165	125	1.03	24.7	165
2	85	60	0.86	27.6	1200
3	50	45	1.54	29.0	315
4	35	NA	1.90	27.6	30
5	50	NA	1.73	27.6	765
6	610	635	1.50	31.1	155
7	475	490	1.87	33.9	70
8	465	340	1.41	29.2	500
9	290	240	1.76	31.5	75
10	300	290	1.76	33.1	70
11	200	120	1.97	34.6	75
12	340	300	1.52	31.1	115
13	300	275	1.63	34.0	75

NA = not available

In Example I:

Run 1 is a comparative run using the polyethylene per se;

Run 2 is a comparative run using the polyethylene and modified polyolefin, in the ratio that corresponds to Runs 7 and 9;

Run 3 is a comparative run of polyethylene and filler but without modified polyethylene, which shows improvements in stiffness and tensile strength over Run 1 but a decrease in impact strength;

Run 4 is a comparative run of polyethylene and untreated filler and shows similar results to Run 3;

Run 5 is a comparative run similar to Run 4 but with a different untreated filler;

Runs 6-13 are runs of the present invention that show major increases in the impact strength of the resultant products in comparison to Runs 1-5. In addition both flexural modulus and tensile strength show increases over polyethylene;

Runs 10-12 are runs of compositions that contain polyamide. The addition of polyamide decreases impact strength but increases tensile strength of the composition.

CLAIMS:

1. A composition comprising:

(a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin, and mixtures thereof;

(b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and

(c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound.

2. The composition of Claim 1 in which the ethylenically unsaturated carboxylic acid is maleic acid and the ethylenically unsaturated carboxylic acid anhydride is maleic anhydride.

3. The composition of Claim 1 or Claim 2 in which a portion of the aluminum silicate has been replaced with another filler.

4. The composition of any one of Claims 1-3 in which a portion of the polymeric component has been replaced with a polar polymer.

5. The composition of any one of Claims 1-4 in which the polyolefin of (a) has a density in the range of 0.920-0.960 g/cm^3.

6. The composition of any one of Claims 1-5 in which the polyolefin of (a) has a melt index in the range of 0.5-20 dg/min.

7. The composition of any one of Claims 1-6 in which the modified polyethylene of (b) has a density of at least 0.920 g/cm^3.

8. The composition of Claim 7 in which the modified polyethylene of (b) has a density of at least 0.950 g/cm^3.

9. The composition of any one of Claims 1-8 in which the modified polyethylene has a melt index in the range of 0.2-2.0 dg/min.

10. The composition of any one of Claims 1-9 in which the amino silane is of the formula R-SiX_3 in which R is an organofunctional group, X is a hydrolysable group and at least one of R and X contains an amino radical.

11. The composition of Claim 10 in which the amino silane is 3-aminopropyl trimethoxy silane.

12. A process for the manufacture of a polyolefin composition, comprising:
(i) feeding to apparatus adapted for the admixing of molten thermoplastic polymers with other materials, an admixture of: (a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin,

and mixtures thereof; (b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and (c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound;

(ii) admixing (a), (b), and (c) at a temperature above the melting point of the polymers of (a) and (b), said temperature being below the temperature of decomposition of both said filler and the polymers of (a) and (b); and

(iii) extruding from the apparatus a composition formed from (a), (b) and (c).

13. A process for the manufacture of articles comprising the steps of feeding a composition to extrusion or moulding apparatus, and forming said article by extruding or moulding said composition into a shaped article and cooling the article so formed, said composition comprising:

(a) 0-80% by weight of the composition of a polyolefin selected from the group consisting of homopolymers of ethylene and copolymers of ethylene with at least one C_3-C_{10} alpha-olefin, and mixtures thereof;

(b) 10-70% by weight of the composition of a modified polyethylene, said polyethylene being selected from

the group consisting of homopolymers of ethylene and co-polymers of ethylene with at least one C_4-C_{10} alpha-olefin, and mixtures thereof, said polyethylene having been modified by grafting at least one of an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated carboxylic acid anhydride onto said polyethylene, such that the resultant modified polyethylene contains a total amount of between 0.05 and 5.0% by weight, based on the weight of polyethylene, of said acid and said anhydride; and

(c) 10-70% by weight of the composition of aluminum silicate, said aluminum silicate having been surface treated with an amino-silane compound.

14. An article when made by the process of Claim 5 or Claim 6.

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